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The ionic liquid (IL) program at the Air Force Research Laboratory is focused on the synthesis and characterization of tailored energy-dense liquids to provide a scientific foundation for the advancement of the performance and operability envelopes of current propulsion systems. General efforts focus on the discovery of energetic ILs based on heterocyclic and open-chain cations in combination with reactive anions. A major goal has been the development of IL fuels which undergo hypergolic ignition upon contact with common propulsion oxidizers. This account discusses the combination of some azolium, ammonium, hydrazinium, guanidinium and hydrazidinium cations with dicyanamide, nitrate, azide and tricyanomethanide anions. Their synthesis and characterization are described along with results of simple hypergolicity drop tests. The utility and reproducibility of these tests and possible mechanistic scenarios for these reactions are also discussed.

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Ionic Liquid Fuels for Chemical Propulsion

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The ionic liquid (IL) program at the Air Force Research Laboratory is focused on the synthesis and characterization of tailored energy-dense liquids to provide a scientific foundation for the advancement of the performance and operability envelopes of current propulsion systems. General efforts focus on the discovery of energetic ILs based on heterocyclic and open-chain cations in combination with reactive anions. A major goal has been the development of IL fuels which undergo hypergolic ignition upon contact with common propulsion oxidizers. This account discusses the combination of some azolium, ammonium, hydrazinium, guanidinium and hydrazidinium cations with dicyanamide, nitrate, azide and tricyanomethanide anions. Their synthesis and characterization are described along with results of simple hypergolicity drop tests. The utility and reproducibility of these tests and possible mechanistic scenarios for these reactions are also discussed.

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Introduction

Despite early mention in the propellant literature (1), energetic ILs are only now receiving increasing consideration as practical rocket propellants. Understanding this trend requires reflection upon the historical context in which our current state-of-the-art propellants were chosen and developed.

The urgency of the Cold War and the race for the moon led to an explosion in resources devoted to rocket propulsion. In these "glory days" large regions of the chemical landscape were explored in the quest for the competitive edge in chemical propulsion. Accounts of this time remain an important resource for today's propellant chemist. In his memoir surveying this work, an American pioneer, John Clark, makes tantalizing mention of ILs in general and ethylammonium nitrate in particular: “Molten salts are nothing new, but these were the only ones I ever heard of that were liquid at 25°C. I’ve never found a use for the ethylamine compound, but something with such interesting properties ought to be good for *something!*” (1)

In addition to providing the impetus for ground-breaking chemical research, the objectives of the time demanded that environmental and health considerations be subjugated to raw performance. It is therefore little wonder that at the time of his writing Clark saw a future for the hydrazine/ClF_5 fuel-oxidizer combination. Although nitric acid (in the form of IRFNA, inhibited red fuming nitric acid) and nitrogen tetroxide were ultimately down-selected as room-temperature oxidizers in preference to the interhalogens, the hydrazines remain the state-of-the-art fuels for non-cryogenic applications.

Another feature that makes hydrazine such a desirable fuel is its hypergolic ignition (the spontaneous ignition upon contact) with most commonly used oxidizers. This type of chemical ignition makes system starts and restarts reliable and minimizes complexity as no additional ignition source is needed. There is a simple, effective method to quickly screen a variety of materials for this desired ignition behavior. The procedure is commonly referred to as a drop test. Typically a drop of fuel is released from a syringe or pipette into a crucible containing an oxidizer and ignition is determined by a high speed video camera, perhaps in combination with measurement of a sudden pressure increase (Figure 1). The ignition delay (ID) time is the interval between the first contact of fuel with oxidizer and ignition. With origins extending back to at least the second world war, this test was the primary initial screening tool in what Clark describes as the "hunt for the hypergol" during the nineteen sixties. It continues despite the wide recognition that its conditions are not perfectly representative of those in a combustion chamber.

Today, well after the Sputnik era, priorities have shifted. Even as ease of ignition is still desirable and higher performance remains a preeminent goal, hazard properties have arisen as more significant drivers of cost and feasibility.

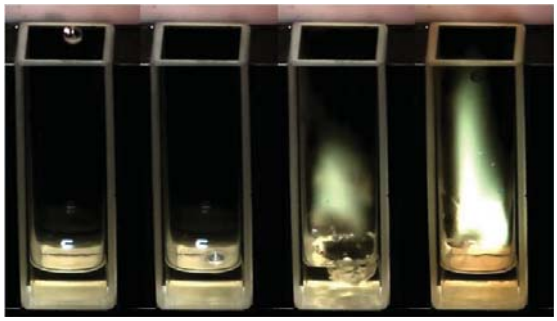


Figure 1. *Drop test: A fuel drop is released from a syringe into the oxidizer.*

Most of the handling difficulties of the noncryogenic fuel/oxidizer combinations are associated with the vapor toxicity of hydrazines. Flammability is also a significant handling and operations issue. Energetic ILs with virtually no vapor pressure and low flammability would seem ideally suited as potential hydrazine replacements.

Ethylammonium nitrate is generally regarded as the first reported room temperature ionic liquid (RTIL). Since it is a nitrate salt, it certainly carries a significant amount of energy and might even be thought of as a promising prototype of a monopropellant. These single component propellants carry the advantages of engineering simplicity associated with the fuel and oxidizer residing in a single tank. However, by itself, ethylammonium nitrate lacks sufficient oxygen to assure balanced combustion to CO, CO_2, H_2O and N_2. The work of Christe (2) and Shreeve (3) begins to overcome this difficulty by introducing multiple nitrato- functionalities into a single molecule. Chemical stability is often sacrificed by this approach and the Air Force's current monopropellant development program (not otherwise discussed in this work) seeks a suitable candidate by partitioning the fuel and oxidizer into separate molecules or ions in a single solution.

In contrast, the present work is primarily concerned with what are referred to as bipropellants in which safety and stability are enhanced by segregating fuel and oxidizer into separate working fluids. Indeed, the substantial history of underoxidized energetic ILs of varying energy content seemed to promise ILs of sufficient energy to undergo hypergolic ignition with common propellant oxidizers. Nevertheless, initial tests with some easily prepared nitrate (NO_3^-), dinitramide ($N(NO_2)_2^-$), and perchlorate (ClO_4^-) salts were disappointing. None yielded a visible flame in drop tests. Even multiple drops in the same test were insufficient to lead to ignition.

At this point, it became clear that new design work would need to be conducted targeting fuel-rich materials with sufficient propensity toward oxidation to support facile ignition. The first class of compounds considered

were ILs incorporating the azide anion, based on the known, exothermic reactivity of simple azides with nitrogen tetroxide (Scheme 1). Various liquid IL azides were prepared but, while exhibiting significant reactivity, they did not undergo hypergolic ignition. Therefore, we considered the investigations unsuccessful (4).

Scheme 1

$$N_2O_4 \rightleftharpoons NO_3^- + NO^+$$

$$N_3^- + NO^+ \rightleftharpoons N_3NO \longrightarrow N_2 + N_2O$$

$$N_2O_4 + N_3^- \longrightarrow NO_3^- + N_2 + N_2O$$

The breakthrough in this research resulted from a serendipitous effort to enhance the physical properties of the ionic liquids. While we recognized that the dicyanamide (dca) anion provides a combustible organic structure, we primarily sought to take advantage of the fact that the dca anion is known to produce ILs with low viscosities and a large liquidus range. Even though dca could not be considered a very high-energy anion, these ILs were subjected to drop test experiments. This resulted in the discovery of the first hypergolic IL family (5, 6). Ever since, many hypergolic ILs have been developed, in our laboratory and elsewhere (7-12), but the majority of these are based on the dca anion.

Our laboratory is continuing to pursue the interesting class of hypergolic ILs, both by themselves and in combination with nanoparticles (13). This work is a summary account of our efforts to devise chemical strategies to discover materials with reduced IDs and improved performance characteristics.

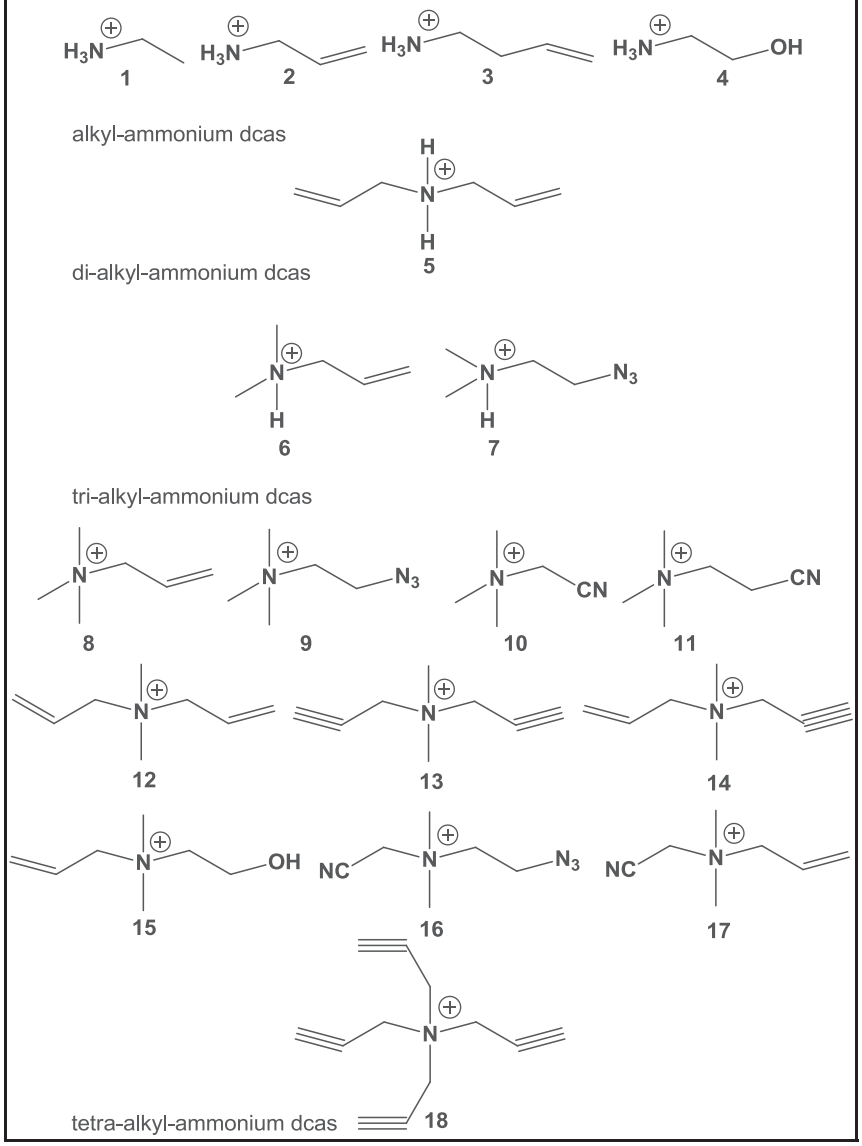
Results and Discussion

Ammonium-based IL dicyanamides

If we follow the accepted definition of an IL, a salt with a melting point below 100°C, the literature provides us with an interesting timeline leading to the development of the first RTIL. One of the first ILs produced was probably hydroxyethylammonium nitrate (mp. 52-55°C) in 1888 (14), followed by hydrazinium azide (mp. 75°C) in 1891 (15) and finally the first RTIL, ethylammonium nitrate (mp. 9°C) in 1914 (16). There are two noteworthy features: all of these first generation ILs are based on open-chain amine cations and all are energetic ILs. Many neutral, open-chain amines have also been considered as potential propellant fuels and their hypergolic reactivity decreases as tertiary > secondary > primary (1).

We chose to study a narrow set of protic and aprotic cations based on commercial availability, and therefore ease of preparation, as well as the presence of potential reactive substituents (Scheme 2).

Scheme 2



A total of seven protic, ammonium-based IL dcas were investigated: four monoalkylated (17), one dialkylated (17, 18), and two trialkylated. An additional eleven were tetraalkyl-ammonium dca salts, six with two different substituents, four with three different substituents and tetrapropargyl-ammonium dca. Their physical properties are listed in Table 1.

Table 1. Physical properties of the ammonium IL dcas.

Compound dicyanamide	**melting point [°C]**	**decomp. onset [°C]**	**Viscosity 25°C [cP]**
1	46	86	[a]
2	11	78	95
3	[b]	75	120
4	14	[c]	106
5	37	71	37[b]
6	[b]	108	[c]
7	16	95	74
8	28	229	26[b]
9	16	187	81
10	122	176	[a]
11	79	113	[a]
12	[b]	200	37
13	74	155	[a]
14	23	172	111
15	-4	193	87
16	[d]	100	[a]
17	35	144	[a]
18	113	147	[a]

[a]solid; [b]supercooled liquid; [c]not determined; [d]not observed

These studies substantiate the difficulty of *a priori* prediction of IL physical properties. Ethylammonium nitrate is well established as a RTIL. Therefore, it was expected that **1** would also be a RTIL, since dcas generally possess lower melting points than their nitrate counterparts. As can be seen from Figure 2 and Table 1, **1** is a solid with a surprisingly high melting point of 46°C. The X-ray crystal structure reveals a strong hydrogen-bond network (Figure 3) but it is not obvious why the general trend is reversed in this case.

About half of the materials were obtained as RTILs with melting points ranging between -4°C to 28°C (Table 1). Furthermore, the liquids manifested acceptably low viscosities between 26cP and 120cP. While the melting points and viscosities appear to be attractive for the protic IL dcas, their low

decomposition onsets render them impractical for propellant applications. In contrast, the fully quarternized ammonium dcas generally showed excellent thermal stability.

Figure 2. *Protic IL dcas* ***1****,* ***2****,* ***3****,* ***4*** *and* ***5****.*

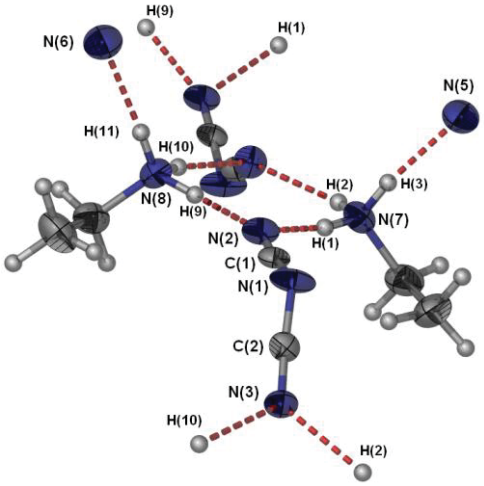


Figure 3. *Molecular structure and hydrogen-bond network in* ***1****. (Thermal ellipsoids shown at 50% probability level)*

Represented by compounds **7** and **9**, the intrinsic thermal stabilities of protic and aprotic IL dcas are illustrated in Figure 4. The TGA study on **9** (isothermal at 75°C) revealed a weight loss of less than 0.2% after 100h compared to over 30% after only 48h for **7**. Compounds **7** and **9** were prepared from the same parent amine, dimethylazidoethyl amine (DMAZ) (**9** was also investigated by

Shreeve (10)). This amine was considered for a time as a replacement for hydrazine in bipropellant applications (19) and, therefore, it seemed ideally suited as a starting point for ammonium ILs.

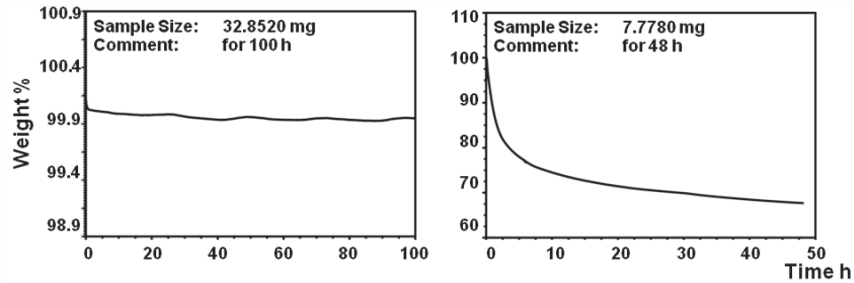


Figure 4. *TGA isothermal at 75°C of* ***9*** *(left) and* ***7*** *(right).*

Reactivity of protic and aprotic IL dcas with WFNA

The next step was to test the reactivity of the ILs towards white fuming nitric acid (WFNA) and measure approximate ID times. Tests with other oxidizers, *i.e.* N_2O_4 (NTO) and 93% H_2O_2 did not produce ignition. Only RTILs **2**, **5**, **8**, **9**, **12**, **14** and **15** were tested because the initial quantities of **3**, **4** and **7** were consumed in characterization. Solids were not tested. The results are presented in Table 2.

Table 2. Hypergolic ignition of ammonium IL dcas with WFNA.

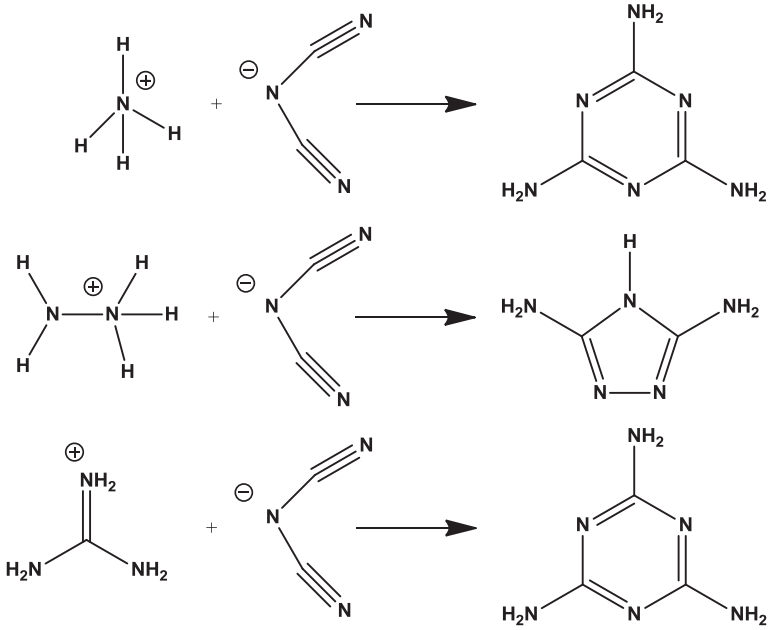
Compound dca	1st test ID time [ms]	2nd test* ID time [ms]	3rd test* ID time [ms]
2	NI[a]	88	97
5	NI	149	185[b]
8	40		
9	34		
12	69		
14	50		
15	NI	198	
23	NI	NI	155[b]

* freshly prepared sample; [a] NI = No ignition; [b] = ignition on second drop

The first test series might lead to the conclusion that protic IL dcas and those containing hydroxyl functionalities are not hypergolic. Protic dca salts are known to undergo cyclization upon heating which could explain the initial drop

test results, as otherwise reactive species are diverted from ignition. Examples in the literature are ammonium and guanidinium dcas forming melamine (20, 21) and hydrazinium dca cyclizing to guanazole (22) (Scheme 3).

Scheme 3



Although these cyclization reactions are exothermic and can lead to explosions, the end products have high melting and decomposition points and are not hypergolic with WFNA (22). Cyclization may compete with condensed phase pre-ignition chemistry of the dca anion. In fact, cyclization products have been found in the residue of the reaction of some IL dcas with WFNA (23).

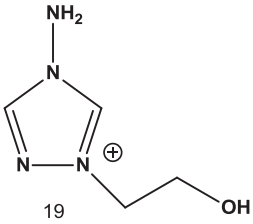
In an effort to substantiate the hypothesis concerning inhibition of ignition by a hydroxyl group, a new IL was prepared, 1-(2-hydroxyethyl)-4-amino-1,2,4-triazolium dca, **19** (Scheme 4). It has a decomposition onset of 154°C and a viscosity of 747cP at 25°C.

An initial test produced a violent reaction but no ignition with WFNA (Table 2). Two more batches were freshly prepared and gave the same negative result. During the third experiment a second drop was inadvertently released from the needle and hit the oxidizer 3016 ms after the first drop. Ignition followed after an additional 155 ms. Ignition might have occurred because of exothermic events following the addition of the first drop.

These results prompted us to reinvestigate ILs **2**, **5**, and **15** which previously gave negative results. While the initial samples had been stored at ambient

conditions for a couple weeks before the drop tests (and may have undergone some preliminary cyclization), freshly prepared samples were immediately subjected to drop tests. All three samples ignited with the first drop (Table 2). A third sample of **2** gave the same result as the second, but for **5** a second drop (arriving 3892 ms after the initial drop) was necessary, with ignition following after 185 ms.

Scheme 4



Before we continue to discuss drop tests in more detail the prevalence of dca cyclization reactions is illustrated by our investigation of hydroxylammonium dca, **20**. The thermally induced cyclization product was reported to be 3,5-diamino-1,2,4-oxadiazole, **21** (Scheme 5) (24). In an attempt to prepare **20** at ambient temperature the NMR spectra still indicated the presence of **21**. The ring structure was confirmed by the single-crystal X-ray structure (Figure 5).

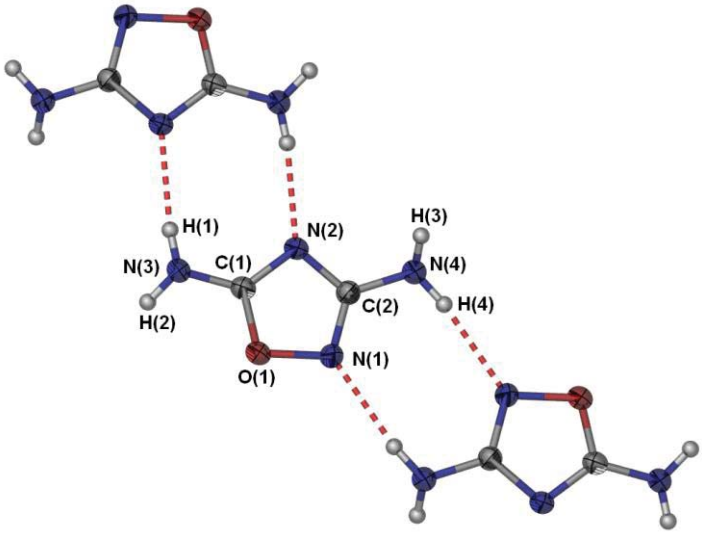
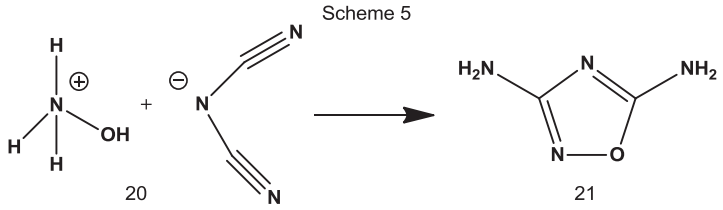


Figure 5. *Molecular structure and hydrogen-bond network of 21. (Thermal ellipsoids shown at 50% probability level)*

Scheme 5



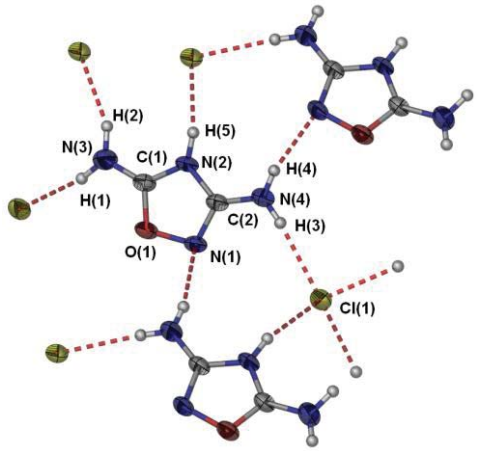


Figure 6. *Molecular structure and hydrogen-bond network of* ***22****. (Thermal ellipsoids shown at 50% probability level)*

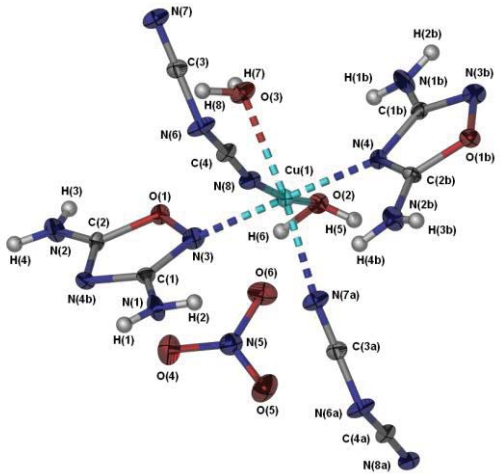


Figure 7. *Molecular structure of* ***23****. (Thermal ellipsoids shown at 50% probability level)*

To further explore the reactivity of this barely investigated diamino-oxadiazole, a simple protonation (25) with HCl as well as reaction with a transition metal salt, $Cu(NO_3)_2 \bullet H_2O$, were carried out. The x-ray structures of the obtained materials, **21** and **22**, are shown in Figure 6 and 7.

Figure 7 illustrates that in **22** the heterocycle coordinates through both ring nitrogens (Figure 7). Contamination with dca is apparent as the Cu-complex incorporates dca anions as well.

Drop test reliability and reproducibility

At this stage it seems appropriate to make some more general remarks about drop tests. In most cases ignition occurred with a marked "pop" sound. Popping phenomena are known in many hypergolic systems where they have been characterized as explosions. Systematic studies have been undertaken to minimize their occurrence in the hydrazine-NTO system (26, 27).

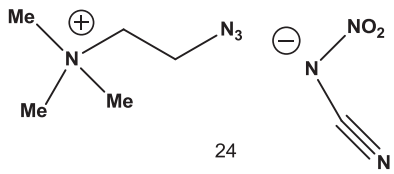
With regard to ID times, different laboratories rarely report the same ID time for the same compound, but they generally agree on the rankings of propellant combinations (1). Being so simple, quick and inexpensive these tests and the rankings obtained from them are an indispensable resource for the propellant chemist, even if they do not definitively measure the intrinsic ID. They are certainly no substitute for subsequent small engine tests to solve "popping" and other potential hard-start issues.

Nevertheless, some simple actions can enhance their reliability and reproducibility and increase confidence in the rankings of IDs determined. In our laboratory the apparatus has been moved into a dedicated drybox with inert nitrogen atmosphere to eliminate interference from atmospheric oxygen and to more reliably assess the reactivity of moisture-sensitive materials. Also the fuel is dropped into a cuvette with a standard 250μL volume of the oxidizer. Hypergolic reactions which require multiple drops for the same oxidizer aliquot do not provide ID data which we regard as significant. Furthermore, a remote-controlled syringe is used to keep the flow rate, height and drop sizes constant for each fuel and a standard IL, **9**, is employed to confirm the quality of the WFNA used for each day's tests. The details of this test and the importance of WFNA purity are discussed later in the chapter.

Many variables influence these drop test results. For example, drop sizes are determined by surface tension, viscosity, etc. Fuel and oxidizer temperature are major factors. In addition, each drop test provides different speed and efficiency of mixing and a variation of the local oxidizer-to-fuel ratio. Whether the fuel or the oxidizer is dispensed from the syringe is also important. In the case of IL dcas, ID times were recorded as short as 15 ms if the fuel is dropped into a pool of oxidizer, but upon reverse addition the ID time can be greater than 1 second (12). An even more subtle effect was observed in the class of IL

nitrocyanamides (nca) exemplified by trimethylazidoethyl nca, **24** (Scheme 6). This material was reported to ignite within 8 ms with WFNA (10), but with our test using a 21 gauge syringe needle, no ignition was observed. Only upon changing to a larger 18 gauge needle, from which presumably a larger drop was released, were we able to observe ignition with an ID time of 156 ms.

Scheme 6



24

Clearly, not all of these effects can be isolated in such simple tests but the data are informative nonetheless. However, our results would seem to caution against over-interpreting single tests. This nearly resulted in mischaracterization of the WFNA hypergolicity of **2**, **5**, **15** and **23**. Similarly misplaced confidence in a single positive result can lead to unwarranted development efforts.

IL mixtures as fuels

Some ammonium dcas (Table 1) are solids and therefore did not meet our initial criteria to be subjected to drop tests. Although liquids can be obtained by melting salts, room temperature liquids are preferred as propellants. The cation of **18** would not be expected to form a RTIL because of its relatively high symmetry.

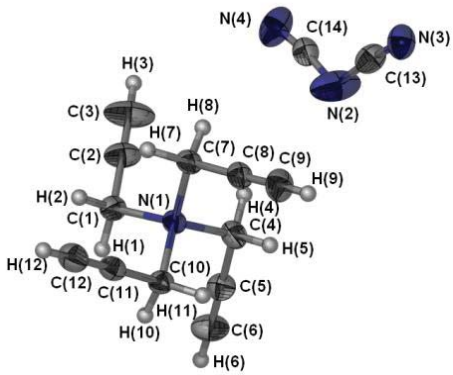


Figure 8. *X-ray crystal structure of 18. (Thermal ellipsoids shown at 50% probability level)*

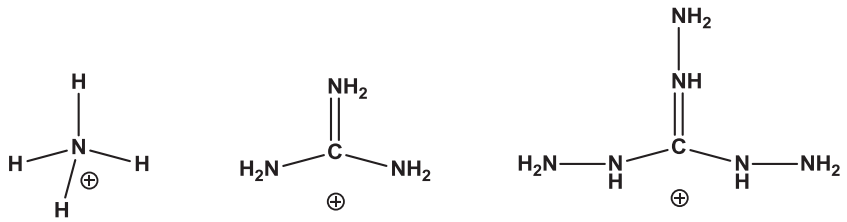
In fact, **18** is a solid at room temperature with a melting point of 113°C, a decomposition onset of 147°C and a density of 1.18 g/cm^3 (Table 1). Its X-ray structure is shown in Figure 8.

Roughly twenty-five weight percent of **18** was dissolved in **9** in the hope, based on the degree of unsaturation, that this mixture would ignite with NTO in addition to WFNA. While the mixture ignited with WFNA, the NTO test was unsuccessful. This strategy of optimizing properties by mixing only partially satisfactory ILs and also the goal of enlarging the range of oxidizers led us to investigate the next class of ILs in an effort to overcome some of the shortcomings of IL dcas.

Higher density dicyanamides

High propellant density is often desirable, especially for small vehicles or spacecraft, improving tank size, overall vehicle weight, cost and system lifetime. Typical IL dcas possess densities between 1.1 and 1.2 g/cm^3. A literature review shows that unsubstituted ammonium (20) and guanidinium dcas (21, 28) can possess densities of 1.3 g/cm^3 or greater (Scheme 7).

Scheme 7



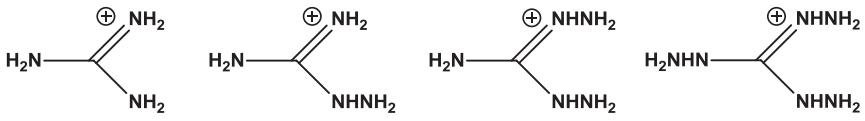
ρ=1.30 g/cm^3 (200K) ρ=1.36 g/cm^3 (200K) ρ=1.42 g/cm^3 (298K)

The substituted ammonium IL dcas have just been addressed, and we investigated the X-ray structure of the unsubstituted hydrazinium dicyanamide, **25** (17, 29). The material showed a melting point (decomposition/transformation onset) of 84°C, within the regime of an IL, and the calculated crystal density is 1.48 g/cm^3 (173K). Among the simple ammonium-, hydrazinium- and guanidinium-dcas, **25** has the highest density. Unfortunately, it easily undergoes thermal cyclization to guanazole (Scheme 3), either in solution or in the solid state (22).

Guanidinium dca, **26** (21, 30-31) and triaminoguanidinium (TAG) dca, **27** (28, 32) have been reported previously. The missing links in the chain of aminated guanidinium dcas are aminoguanidinium, **28** and diaminoguanidinium

(DAG), **29** dcas (Scheme 8). Their single-crystal X-ray structures are given in Figure 9.

Scheme 8



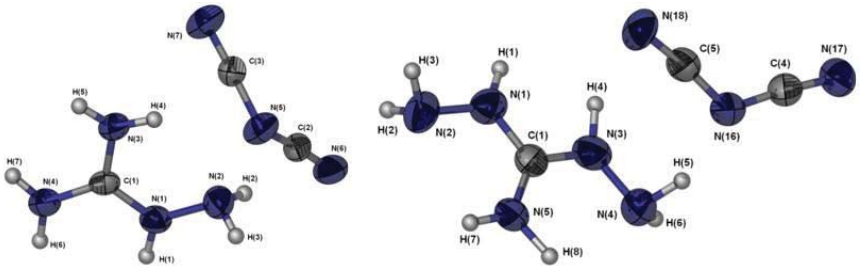


Figure 9. *X-ray crystal structure of* ***28*** *(left) and* ***29*** *(right) (Thermal ellipsoids shown at 50% probability level)*

As can be seen from Table 3 all the guanidinium dcas are solids at room temperature. Furthermore, like the protic ammonium dcas, they show only marginal thermal stability as is evidenced by low decomposition onsets.

Table 3. Physical properties of guanidinium dcas.

Compound dca	melting point [°C]	decomp. onset [°C]	Density ρ [gcm^{-3}]
26[a]	57	145	1.38
28	55	120	1.41
29	61	112	1.36
27[b]	124	150	1.42

[a] ref 21, [b] ref 28

Since three of the four salts have melting points considerably below 100°C we decided to subject them to drop tests (Table 4). The salts were heated until clear liquids were obtained. Ignition was observed between NTO and **29** but not **26** and **28**. **26** is known to undergo cyclization upon heating which might have been partially responsible for its negative results (Scheme 3). Repeating these tests

with the solid guanidinium salts did not yield ignition. Therefore, preheating possibly lowered the activation barrier toward ignition. In the context of our drop test caveats, we do not intend to label the ignition of melted salts as hypergolic (and refrain from giving misleading ID times). Nevertheless we present them as justification for seeking hypergolic RTIL mixtures with these ILs as additives. Accordingly, a mixture of **29** and **9** (0.57 : 1.00 molar ratio) was prepared. The mixture had a viscosity of 139cp and ignited with NTO, but the ID time was too long to justify further propellant development (Table 4).

Table 4. Ignition tests of melted guanidinium dcas towards WFNA and NTO.

Compound Dca	WFNA	NTO
26	NI[a]	NI
28	NI	NI
29	I[b]	I
9/29 1.00 : 0.57[c]	I	I

[a] NI = no ignition; [b] I = ignition; [c] liquid mixture

Given the encouraging test results, the question of whether DAG might be a "trigger" for ignition with different oxidizers was addressed by preparing two other salts, DAG tricyanomethanide (tcm), **30** and DAG azide, **31**. The tcm anion was chosen because TAG tcm has been reported as being hypergolic with NTO (33), while **31** was previously mentioned in the context of explosives and propellants (34-37).

30 has a melting point of 90°C and a decomposition onset of 189°C. **31** is a high-nitrogen compound (84.8 wt%) with a melting point of 109°C and its excellent thermal stability (decomposition onset 187°C) can be explained by the extensive hydrogen bonding observed in the crystal structure (Figure 10).

To avoid the use of silver azide in the production of **31**, DAG tetrafluoroborate, **32** was prepared and treated with potassium azide in IPA according to Scheme 9. Both DAG salts were heated to clear liquids and drop tests were performed (Table 5).

Scheme 9

32 31

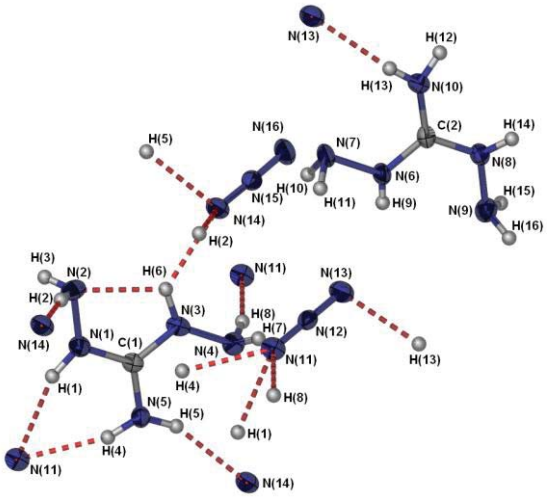


Figure 10. *Molecular structure and hydrogen-bond network of* ***31*** *(Thermal ellipsoids shown at 50% probability level)*

Given the many examples reported, it is reasonable to suppose that it is the dca anion which is responsible for the ignition of IL dcas with WFNA and that the cation plays only a secondary role, influencing the ID time. Our investigations so far indicate that ignition with NTO might be more complex, explaining why only a few hypergolic salts have been found. A successful design path may require particular features on both the cation and anion.

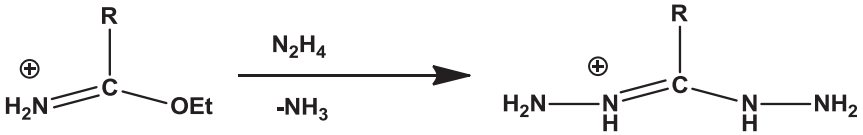
Table 5. Ignition tests of melted DAG salts **29**, **30** and **31**.

Compound	WFNA	NTO
29	I[a]	I
30	NI[b]	I
31	NI	NI

[a] I = ignition; [b] NI = no ignition

The hydrazidinium cation not only bears a similarity to the DAG cation but it also opens design space by substitution of the central carbon (Scheme 10).

Scheme 10



Methylhydrazidinium chloride **33** (38), nitrate **34**, dca **35** and tcm **36** salts were prepared and their X-ray crystal structures are depicted in Figures 11 and 12. These are not RTILs, but they were also subjected to drop tests, either as solids or heated liquids (Table 6).

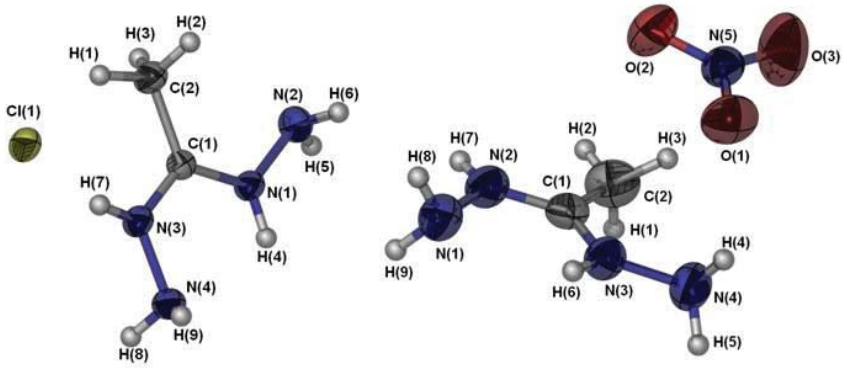


Figure 11. *X-ray crystal structures of* ***33*** *and* ***34*** *(Thermal ellipsoids shown at 50% probability level).*

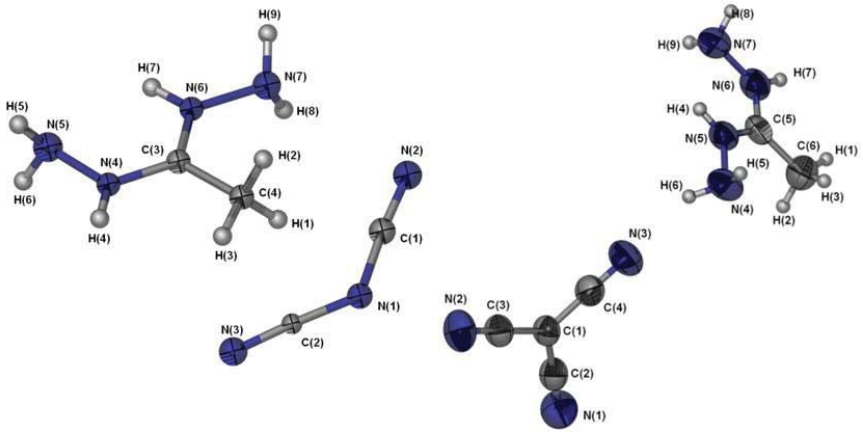


Figure 12. *X-ray crystal structures of* ***35*** *and* ***36*** *(Thermal ellipsoids shown at 50% probability level).*

The reactivity of the hydrazidine salts is quite similar to that observed for the DAG salts. While tests of the chloride and nitrate were negative, molten samples of **35** and **36** ignited with NTO. Unfortunately, preliminary investigations showed that longer alkyl chains lead to decreased thermal stability.

Table 6. Ignition tests of liquid or solid **33**, **34**, **35** and **36**.

Compound	WFNA	NTO solid salt	NTO liquid salt
33	NI[a]	NI	ND[b]
34	NI	NI	NI
35	I[c]	NI	I
36	NI	NI	I

[a] NI = no ignition; [b] ND = not determined; [c] I = ignition

Some mechanistic considerations

The initial discovery of the hypergolic reactivity of IL dcas with WFNA generated some interest in the pre-ignition reaction chemistry. Inspired by some studies on mono- and dinitrobiuret by Thiele (39) and later Klapötke (40), a mechanism was proposed, in which the first step is nucleophilic attack of the nitrate anion on the triple-bound carbon (6). Initial mechanistic experiments were based on two assumptions: that the nitric acid used is indeed 100% nitric acid and that the ionic liquids tested are free of dissolved impurities.

100% nitric acid is a highly complicated system. Nominally nonaqueous nitric acid autodissociates to form small amounts of $H_2NO_3^+$ which, itself, decomposes into its anhydride and water, further shifting the equilibrium to the right (Scheme 11) Thus nitric acid always contains some water and the water leads to formation of additional ions (Scheme 12).

Scheme 11

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$
$$H_2NO_3^+ \rightleftharpoons H_2O + NO_2^+$$
$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

Scheme 12

$$H_2O + HNO_3 \rightleftharpoons H_3O^+ + NO_3^-$$
$$3HNO_3 \rightleftharpoons H_3O^+ + NO_2^+ + 2NO_3^-$$

Purity is a major issue in IL research, since it is well established that impurities dramatically change physical properties. While we were satisfied with the purity of our ILs, we became interested in the effect of diluting the oxidizer or fuel with water or other solvents. As a practical matter the addition of water to a fuel has been used to decrease the combustion temperature.

Two IL hypergols, 1-butyl-3-methyl imidazolium (BMIM) dca and **9**, were diluted with either water or methanol. **9** continued to ignite with water dilution beyond 20 wt% and below a diluent concentration of 14 wt% there was no noticeable effect on the ID (Figure 13).

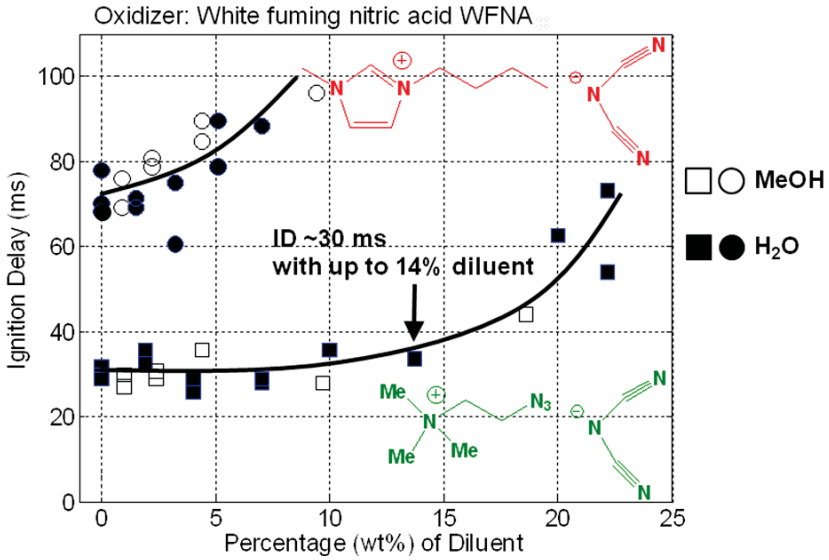


Figure 13. *Influence on WFNA ID time of dilution of BMIM dca and* ***9****.*

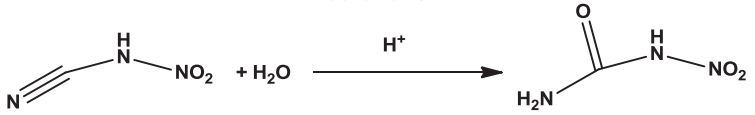
However, when the oxidizer was diluted with water, ignition depended more strongly on which IL was used. A commercial sample of BMIM dca showed no ignition with 96% nitric acid whereas **9** still ignited with 90% nitric acid.

That the quality of the WFNA is of crucial importance for the ID time was already understood in the 1950's (1). This justifies our daily check of WFNA quality using **9**. We have accumulated over 100 ID times on this material varying between 20 and 40 ms. An ID outside of this interval (we have recorded delays of up to 300ms) necessitated replacement of WFNA with a fresh sample. We suspect acid quality as a main culprit for the varying ID times reported by different laboratories. We further think it might be advisable for future nitric-acid work to focus on stabilized IRFNA rather than WFNA, especially since IRFNA is the preferred nitric acid for propellant applications.

Since IL dcas maintain their hypergolicity towards WFNA with substantial dilution, it seems reasonable that water may play a more active role in the ignition mechanism. An investigation of nitrocyanamide decomposition in strong mineral acids established that the acid-catalyzed decomposition involves

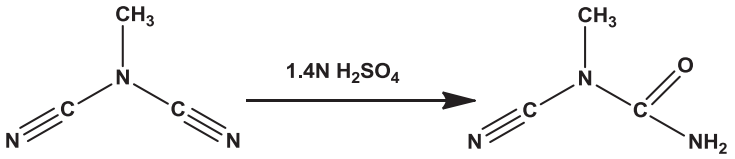
the cyano group (41). The formal addition of H_2O across the CN triple bond was observed with formation of nitrourea (Scheme 13).

Scheme 13



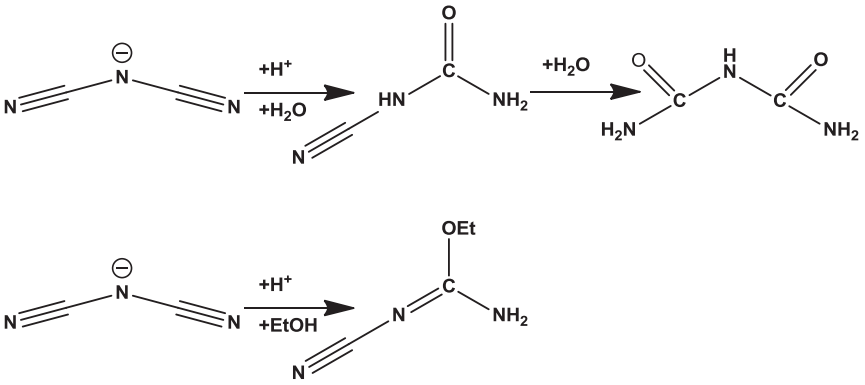
Additionally alkyldicyanamides selectively add water across the CN triple bond in both 1.4N and 12.3N sulfuric acid (Scheme 14) (42, 43).

Scheme 14



Furthermore, it has been demonstrated that sodium dca reacts with HCl, HBr and HI in aequeous solutions to give cyanourea and biuret, while in alcoholic solutions O-ethyl-N-cyanourea is formed (Scheme 15) (44).

Scheme 15



In one of our IL dca samples we found an impurity that was identified as O-methyl-N-cyanourea, **37**, (Figure 14) which formed by the addition of a solvent molecule (methanol) across one dca CN triple bond.

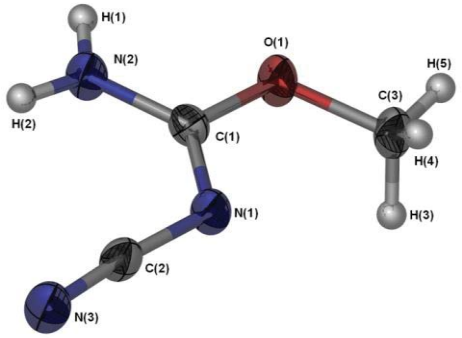
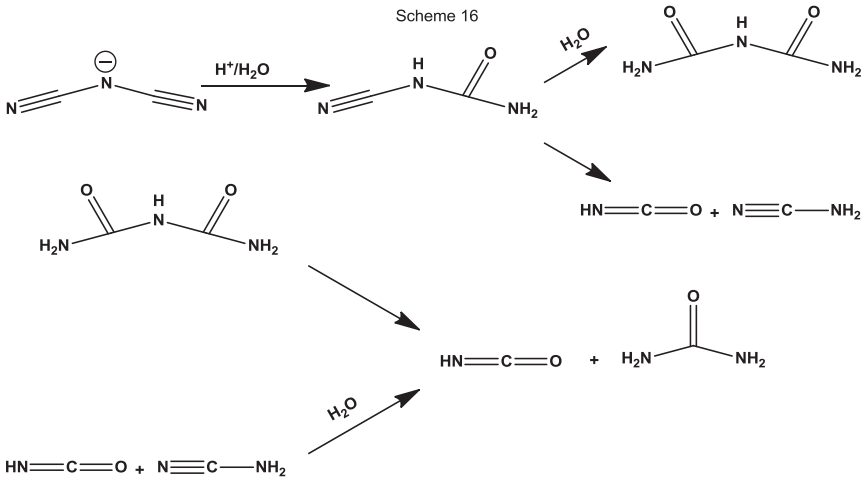


Figure 14. *X-ray crystal structure of* ***37*** *(Thermal ellipsoids shown at 50% probability level).*

Thus, based on our dilution results and literature reactions we propose the mechanism shown in Scheme 16. The action of water leads to the formation of the proposed products cyanourea, biuret, isocyanic acid, cyanamide and urea. Corresponding biuret derivatives have also been observed in the reaction of alkyldicyanamides with sulfuric acid (43). The formation of the end products previously identified (6), like the nitrobiurets, N_2O and CO_2, may also arise by further reaction of these intermediates with nitric acid.

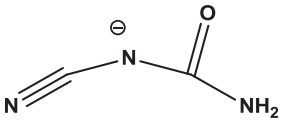
Scheme 16



One of the anions which could initially be formed during an acid-catalyzed addition of water to the dicyanamide anion is the cyanoureate anion (cu) (Scheme 17). BMIM cu, **38** was prepared and obtained as a highly viscous liquid. Drop tests with WFNA revealed no hypergolic properties and so it seems

that the hypergolic reactivity of dca has been tamed by the addition of water across the CN triple bond.

Scheme 17



In the hope of obtaining a more suitable liquid, trimethylazidoethyl ammonium cu, **39** was prepared but was obtained as a solid with a melting point of 105°C (Figure 17) (*c.f.* its corresponding dca, **9**, an RTIL with a melting point of 16°C, Table 1).

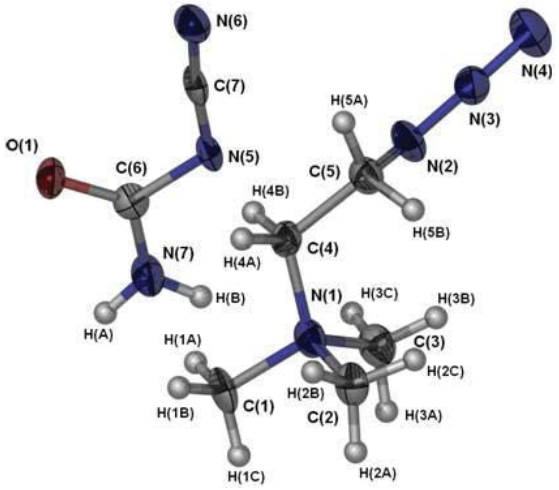
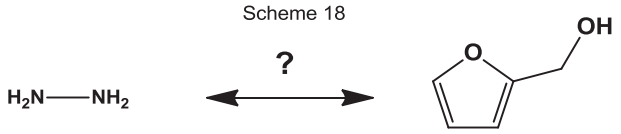


Figure 17. *X-ray crystal structures of **39** (Thermal ellipsoids shown at 50% probability level).*

Current and future directions

Our "hunt for the hypergol" (1) continues to be a rollercoaster ride with flaming surprises as well as disappointing splashes. Designing ILs which fulfill all the other requirements for propellants is, in itself, a difficult task; adding the requirement of hypergolicity only compounds the problem. This should not be too surprising when one compares some of the products of previous searches. For example, there appears to be little structural similarity between hydrazine and furfuryl alcohol (Scheme 18), yet both are hypergolic with several oxidizers.

Scheme 18



Especially puzzling is the fact that many other materials containing directly bound nitrogens or furans with various pendant groups show no hypergolicity. While our discovery of hypergolicity in a new class of single-component RTILs opened new regions of the chemical landscape, a great deal of work remains to satisfy the additional requirements of physical properties, stability, and energy density.

Hydrogen peroxide in concentrated aqueous solution might be an alternative hypergolic oxidizer for some systems. It is attractive for its environmentally benign decomposition products and relatively small ambient vapor pressure. A large part of our current effort focuses on ILs incorporating boro-aluminum hydride scaffolds, but we continue to pursue systems limited to C, H, N and O atoms because many applications require particle-free combustion.

Constrained to this part of the periodic table we are still working to overcome the current limitations of most known hypergols to nitric acid. Relatively few have been found to be hypergolic with higher performing N_2O_4. Although N_2O_4 is highly toxic it is much less corrosive than nitric acid, and therefore easier to handle and we hope to find more IL partners for this oxidizer. We expect fuel mixtures to play a prominent role, not only in tuning the material properties, but also surmounting the difficult ignition barrier.

In pressing our quest to fulfill the promise of ILs as unique, energy-dense fuels, we draw on chemical propellant history while maintaining a healthy respect and skepticism for the value and limitations of simple drop tests. We expect that the route to practical fuels lies not so much in the discovery of a definitive "magic trigger group" but in the careful combination of particular structural features on both the cation and the anion, perhaps in solutions. Our experience with NTO hypergolicity indicates that the cation cannot be completely ignored, but anions may be more determinative of hypergolicity and higher energy content.

Experimental

Starting materials were purchased from either the Aldrich Chemical Company, Inc. or TCI America and were used without further purification. Noncommercial ammonium halide salts were prepared by standard alkylation procedures from the free amine and appropriate alkylhalide following the methods described in (45). Metathesis reactions were carried out according to the general procedure of (5) using silver salts of the anions. When nitrate salts

are prepared exact stoichiometry is essential. 20 was prepared according to (24). 21 was prepared by passing gaseous HCl through a methanol solution of 20. 22 was prepared according to (47), but using 20 instead of DAF. The hydrazidinium halides were prepared according to (38). The purity of all materials was confirmed by NMR spectroscopy.

Nonvolatile solids and liquids were handled in the dry nitrogen atmosphere of a glovebox. The ^{1}H and ^{13}C spectra were recorded on a 400 MHz Ultrashield™ spectrometer at room temperature using 5mm NMR tubes. Glass transition temperatures, melting points and decomposition onsets were determined by differential scanning calorimetry using a Thermal Analyst 200, Dupont 910 Differential Scanning Calorimeter. Measurements were carried out at a heating rate of 10°C/min in sealed aluminum pans with a nitrogen flow rate of 20mL/min starting at -100°C. Thermal gravimetric analysis was carried out using a TA TGA Q5000 instrument holding the sample in a nitrogen atmosphere isothermally at 75°C for 48h or 100h. The single-crystal X-ray diffraction data were collected on a Bruker 3-circle-platform diffractometer equipped with a SMART APEX 2 detector with the χ-axis fixed at 54.74° and using CuK_{α} or MoK_{α} radiation from a fine-focus tube. The goniometer head, equipped with a nylon Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil. The data collection as well as structure solution and refinement were carried out using standard procedures with the APEX2 V.2.1-4, SMART V.5.622, SAINT 7.24A, SADABS, and SHELXTL software packages and programs (46). CCDC-xxxxxx, 1; CCDC-xxxxxx, 18; CCDC-xxxxxx, 20; CCDC-xxxxxx, 21; CCDC-xxxxxx, 22; CCDC-xxxxxx, 28; CCDC-xxxxxx, 29; CCDC-xxxxxx, 31; CCDC-xxxxxx, 33; CCDC-xxxxxx, 34; CCDC-xxxxxx, 35; CCDC-xxxxxx, 36; CCDC-xxxxxx, 37; CCDC-xxxxxx, 39 comprise the supplementary crystallographic data for this paper. They can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

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